

(19)



Europäisches Patentamt
European Patent Office
Offic européen des brevets

(11) Publication number:

0 067 060
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 82302919.4

(51) Int. Cl.³: **B 05 D 1/26, B 05 D 7/14,**
B 32 B 15/08, B 32 B 31/30

(22) Date of filing: 07.06.82

(30) Priority: 09.06.81 JP 88536/81

(71) Applicant: **TAIYO STEEL CO., LTD.**,
1-6 Nihonbashihoncho, Chuo-ku Tokyo (JP)

(43) Date of publication of application: 15.12.82
 Bulletin 82/50

(72) Inventor: **Ayusawa, Saburo, 3-12-20 Shoen, Suginami-ku Tokyo (JP)**
 Inventor: **Minami, Motoichi, 14 Niban-cho, Chiyoda-ku Tokyo (JP)**
 Inventor: **Kameya, Toru, 3-14-D6 Ichikawaminami, Ichikawa-shi Chiba-ken (JP)**

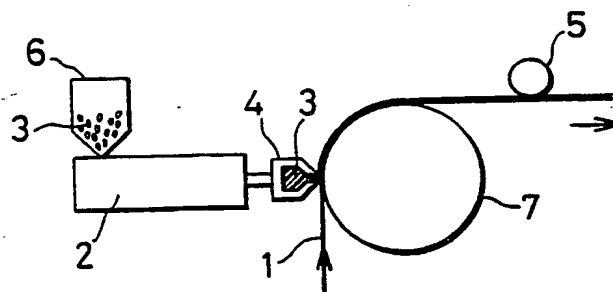
(34) Designated Contracting States: DE GB NL

(74) Representative: **Armitage, Ian Michael et al, MEWBURN ELLIS & CO. 2/3 Cursitor Street, London EC4A 1BQ (GB)**

(54) **Surface treated metal plate and method of producing it.**

(57) A coated metal plate is obtained by extruding thermoplastic resin (3) from a die (4) directly onto a preheated metal plate (1). The surface of the plate can optionally be chemically pretreated, and an adhesive layer may be provided between the metal and the thermoplastic layer, for example by co-extruding it with the thermoplastic resin.

The coated metal has superior anti-corrosion properties and appearance, and can be used in many different fields.



EP 0 067 060 A1

SURFACE TREATED METAL PLATE AND METHOD OF PRODUCING IT

This invention relates to metal plates which are coated with a thermoplastic resin, for example to give anti-corrosion properties and improved appearance.

It has been known to provide a synthetic resin coating for a metal plate by coating a steel plate with a thermosetting acrylic resin paint, or by laminating a pre-formed resin film to a steel plate. Such treated plates are used in many fields, such as building, interior decoration of vehicles, construction of domestic electrical machinery and tools, furniture and other domestic products, particularly because of their attractive colour, appearance and anti-corrosion properties.

However, paints employ resins of relatively low molecular weight, and it is difficult to attain a high molecular weight by baking and curing after coating, and also the fluidity of the paint on the metal plate is usually inadequate, and the coating lacks durability.

On the other hand, in lamination-coating of steel panels, the preformed resin films are produced by extruding resins such as polyvinyl chloride, acrylic resins or fluoroplastics from high molecular weight stock originating in the processes used for their production at petrochemical plants. Thus the molecular weight of such films can be far higher than those obtained from paints. Consequently, the durability of the film on the metal plate is much longer; for example 10 to 20 years as compared with 3 to 5 years for paint coatings.

However, there are problems with such laminated panels.

(i) With very thin films it is difficult to achieve uniform lamination on the metal plate, and wrinkling can occur. For this reason the film thickness is not usually less than 50μ .

(ii) The surface of the metal plate will have microscopic unevennesses, and this tends to produce gaps between the film and the metal plate, so that adhesion of the film can be insufficient.

5 (iii) Since the resin must be preformed as a film, the range of resins which can be used is restricted according to their film-forming ability.

 The present invention is based upon the discovery that a coated metal plate having an attractive appearance
10 and also good adhesion between the coating and the plate and good anti-corrosion properties, as compared with painted and laminated steel plates, can be obtained by extruding a thermoplastic resin directly and continuously onto a pre-heated metal plate. Since the resin is applied directly
15 from the extrusion die in the molten state, without forming it into an independent film, the thickness of the film can be less than 50μ ; preferably from 35μ down to 5μ . The actual thickness of the film used may be determined by the degree of durability required, and also by considerations of
20 cost. The present invention enables the product to be much better matched to these requirements. Furthermore, although hard resins can be used to produce a self-supporting film, the film is easily broken and is difficult to adhere under pressure to the metal plate. In the present invention such
25 hard resins can be used, as they are coated while in the molten state. Moreover, since the step of forming an independent film is omitted, the cost of producing the coated metal is reduced.

 The metal plates which can be coated in accordance
30 with the present invention include steel, zinc-plated steel, zinc alloy-plated steel, lead-plated steel, lead alloy-plated steel, aluminium-plated steel, aluminium alloy-plated steel and stainless steel. As well as purely metal plate substrates, there can be used metal plates which have a
35 surface treatment provided by a chemical layer of about

0.1 - 5 μ . The object of the chemical treatment of the surface is to increase its anti-corrosion, anti-oxidation and adhesion properties. Such treatments may for example include zinc phosphate treatment, iron phosphate treatment, or electrolytic chromate treatment. Additionally or alternatively, the metal plate may have an adhesive layer applied to it. The adhesive layer is at least a few μ thickness, and its object is to increase the adhesion of the subsequently applied thermoplastic resin to the metal plate. Preferred adhesives are thermoplastic resin adhesives having functional groups, for example modified polyethylene, modified epoxy resin and modified vinyl resin. They have good adhesive properties both for metal and thermoplastic resins. They include for example modified polyolefin resins such as ethylene-vinyl acetate copolymer or acrylic acid copolymer in the case of polyolefin-coated steel.

Suitable thermoplastic resins used for coating the metal surface include for example polyolefins, acrylic resins, polyesters, polyamides, polyvinyl chloride, fluorocarbon resins, polycarbonates, styrene type resins, ABS resins, chlorinated polyethers and urethane resins. Polyolefins includes polymers or copolymers of ethylene, propylene, 1-butene or 1-pentene. Acrylic resins include polymers or copolymers of acrylic acid, methacrylic acid, acrylic acid ester, methacrylic acid ester or acrylamide. Polyesters include polyethylene terephthalate and oil-free polyesters. Polyamide resins include so-called nylon 66, nylon 6, nylon 610 and nylon 11. Polyvinyl chloride includes homopolymers and copolymers, for example with ethylene or vinyl acetate. Fluorocarbon resins include tetrafluorinated polyethylene, trifluorinated monochlorinated polyethylene, hexafluorinated ethylene-propylene resin, polyvinyl fluoride and polyvinylidene fluoride.

Mixtures of two or more resins can be used. The film may include conventional additives, for example

anti-deterioration agents, modifiers and pigments. Cross-linking agents such as amino resins or epoxy resins can be added so long as fluidity of the coating is not lost.

The thermoplastic resin is selected according to the requirements of weatherproofing properties, durability to extremes of cold or heat, anti-scratch properties, anti-contamination properties, chemical durability, ease of processing in deep-drawing, and other objects in having a coated metal plate. For example, polyolefin is superior in its resistance to extremes of cold. Polyamide is superior in its abrasion-resistance. Acrylic resin is superior in its contamination-resistance and also chemical resistance. Fluorocarbon resin is superior in its weatherproof properties.

Resins can be coated forming a mono-layer or multi-layers of the same or different resins. In the case of multi-layer coatings, a multi-layer die can be used, optionally providing an adhesion layer between thermoplastic layers.

For example, a multi-layer coated steel plate can be directly and continuously produced by extruding a molten thermoplastic resin as a lower layer, a molten adhesive resin as a middle layer, and another molten thermoplastic layer as an upper layer, the films being produced by a three-layer T-die onto a steel plate which has been precoated with an adhesive and has been preheated. Alternatively, a coated steel plate can be directly and continuously obtained by extruding a molten adhesive resin as a first layer, a molten thermoplastic resin as a second layer, and a molten adhesive resin as a third layer, and a molten thermoplastic resin as a fourth layer; all four films being produced from a four-layer T-die onto a preheated steel plate.

To give a more specific example, a zinc-plated steel

plate or cold rolled steel plate can have a chemically treated surface layer on which is applied an adhesive coating and a coating of polyolefin on the adhesive layer. This has good cold-resistance and durability, and low friction with respect to snow, and thus is suitable for outdoor use in cold districts, for example in providing roofs or walls of buildings.

5 A steel plate having a fluorocarbon resin layer on a polyolefin layer with an adhesive layer in between has very good weatherproof properties.

10 A steel plate having a flame-retardant resin layer applied through an adhesive layer onto a foamed urethane resin layer which in turn is secured to the chemically treated surface of a cold rolled steel plate through an adhesive layer has good heat-insulation and flame-retardant properties, and is thus suitable for interior decoration panels.

In another example an adhesive layer is applied to a chemically treated cold rolled plate, a polyolefin layer is applied to the adhesive layer, an adhesive layer is coated onto the polyolefin layer, and a polycarbonate layer is coated onto the adhesive layer. This coated metal plate is suitable for domestic electrical appliances, because of its scratch-resistant properties.

25 The foregoing multi-layer coated surfaces can be produced using multi-layer T-die .

In coating an adhesive onto a metal base plate, spray coating or roll coating can be used when the adhesive is solvent-based. When the adhesive is of a powder type a fluidised immersion method, electrostatic spray method, electrostatic atomisation method, or flame-spraying method may be used. When the adhesive is in pellet form the multi-layer extrusion method may be used.

It is necessary to heat the metal base plate in advance of applying the molten resin. Without preheating

the adhesion of the resin is inadequate, and hence for example the anti-corrosion property may be adversely affected. Higher preheating temperatures are preferred as this increases the fluidity of the resin, but the
5 temperature should not be so high as to produce decomposition of the resin or adhesive, and moreover it is wasteful of energy. Preferably preheating is at a temperature below that of the molten resin, preferably at least 50°C below the temperature of the molten resin.
10 Usually the preheating temperature is in the range 50 - 250°C.

The invention will be more particularly described with reference to the accompanying drawings, wherein:

Fig. 1 is a diagrammatic representation of a process for coating using a T-die close to a metal plate;

15 Fig. 2 is a diagrammatic representation of a process for coating in which the T-die is spaced from the metal plate and a press roll is applied;

Fig. 3 is a diagrammatic representation of a process for coating by downward extrusion of resin into a nip
20 between a metal plate and a cold roll.

Referring to Fig. 1; a resin 3 from a hopper 6 is melted and mixed in an extruder 2 and is extruded to form a film at the outlet of a T-die 4, the mouth of which is closely adjacent the surface of a preheated metal plate 1
25 which is moving around a guide roll 7. The coated metal plate then passes under a press roll 5 to press down the surface coating. The resin is extruded in the molten state, but it should not only have fluidity but also some tackiness. It should be sufficiently molten such that if
30 two such resins or a resin and metal plate are pressed together by hand they cannot be easily peeled apart.

Fig. 2 shows the extrusion die 4 somewhat spaced from the surface of the metal plate 1, and the extruded resin is deposited on a horizontally moving surface of the plate,
35 where it is immediately pressed down by passing it under

the press roll 5.

In the embodiment shown in Fig. 3, the metal base plate 1 is passed around a heating roll 8 and then around a cold roll 9. The molten thermoplastic film is extruded from the die 4 downwardly onto the heated surface of the metal plate in the nip between the plate and the cold roll 9. The diagram also illustrates the use of two extruders 2 so as to produce a two-layer extruded film. This process enables easy control of the film thickness and the surface finish. For example, it is easy to control the surface gloss and to add an embossed pattern on the surface.

The metal plate 1 coated at high temperature by molten resin 3 is subsequently cooled and rolled. Any suitable cooling method can be used, for example by passing through a cooling vessel or between cooling rolls.

The invention will be more particularly illustrated by the following Examples 1 to 10 and Comparative Examples 1 to 3.

20

EXAMPLES 1 to 10

A metal base plate is prepared by chemically treating a zinc-plated steel plate of 0.4 mm thickness with zinc phosphate. The surface-treated metal plate is coated with resins by the method shown in Fig. 1, and was subsequently tested, given the results shown in Table 1. In the case of polyethylene, the temperature of the extruded resin was about 250°C.

COMPARATIVE EXAMPLES 1 to 3

30

A metal base plate which had not been previously heated was used in Comparative Example 1; a commercially obtained steel plate having a baked coloured acrylic paint coating was used in Comparative Example 2; and a commercially available polyvinyl chloride-laminated steel plate was used in Comparative Example 3. They were tested in the same

manner as Examples 1 to 10, and the results are also shown Table 1.

Further tests were done as follows.

- 5 (i) Adhesion. The coating layer was cut through to the metal plate, and its appearance was observed after peeling the coated layer at the rate of 50 mm/min. For coated layers of 50 μ or less, the peeling was done after applying a tape to it.
- 10 (ii) Corrosion resistance. Degrees of corrosion were observed after spraying with 5% sodium chloride aqueous solution on test panels at 35°C for 10,000 hours.
- 15 (iii) Weather resistance. The condition of the surface was observed after leaving test panels in a weathermeter for 1000 hours.
- (iv) Appearance. The surface appearance was observed and the results shown in the Table according to the following standard.

20

- * Excellent
- O Very Good
- A Good
- X Bad

25 From the foregoing it will be seen that coated metal plates of the present invention have superior properties as compared with conventional coated metal plates, and moreover it is possible to apply a thin coating, and the coating process has been simplified.

30

TABLE 1

	Kind of resin	Thickness μ	Preheating temperature	Kind of adhesive	Appearance	Adhesion	Corrosion resistance	Weather resistance
Example 1	Polyethylene	200	170°C	Modified polyethylene	O	*	*	O
Example 2	Polyethylene	50	170°C	Modified polyethylene	O	*	*	O
Example 3	Polyethylene	30	170°C	Modified polyethylene	O	*	*	O
Example 4	Polyethylene	10	170°C	Modified polyethylene	O	*	O	O
Example 5	Polypropylene	50	170°C	Modified polyethylene	O	*	*	O
Example 6	Polyvinyl chloride	30	170°C	Modified epoxy resin	O	*	O	Δ
Example 7	Vinylidene fluoride	30	170°C	Modified epoxy resin	O	*	*	*
Example 8	Vinylidene fluoride	10	170°C	Modified epoxy resin	O	*	*	*
Example 9	Polyethylene	30	250°C	Modified polyethylene	O	*	*	O
Example 10	Polyethylene	30	50°C	Modified polyethylene	O	O	*	O
Comparative Example 1	Polyethylene	30	Room temperature	Modified polyethylene	O	Δ	Δ	Δ
Comparative Example 2	Acrylic resin	15	-	-	O	Δ	X	X
Comparative Example 3	Polyvinyl Chloride	200	-	-	O	Δ	Δ	O

CLAIMS:

1. A method of producing a coated metal plate, characterised in that it comprises heating the metal plate
5 (1) and directly extruding a thermoplastic resin (3) onto the heated surface.
2. A method according to claim 1 wherein the metal plate is steel, metal-plated steel or stainless steel.
3. A method according to claim 1 or claim 2 wherein the
10 metal plate has a chemically treated surface layer.
4. A method according to any one of the preceding claims wherein an adhesive layer is located between the thermoplastic resin and the metal.
5. A method according to claim 4 wherein the adhesive
15 layer is extruded with the thermoplastic resin from a multi-layer die.
6. A method according to any one of the preceding claims wherein at least two thermoplastic resin layers are extruded onto the metal plate from a multi-layer die.
- 20 7. A method according to claim 6 wherein an adhesive layer is co-extruded between adjacent thermoplastic resin layers.
8. A method according to any one of the preceding claims wherein the metal plate is preheated to a temperature below that of the extruded resin.
- 25 9. A method according to claim 8 wherein the metal is preheated to a temperature at least 50°C below that of the extruded resin.
10. A metal plate (1) coated with a thermoplastic resin (3) characterised in that the resin has been directly
30 extruded onto the plate.

FIG. 1

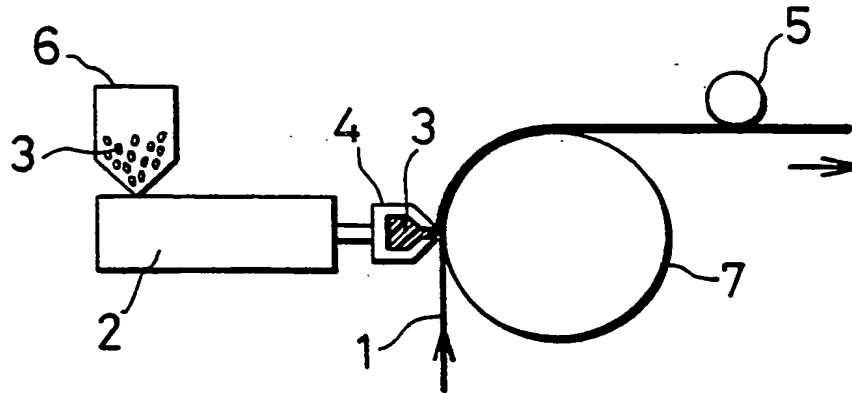


FIG. 2

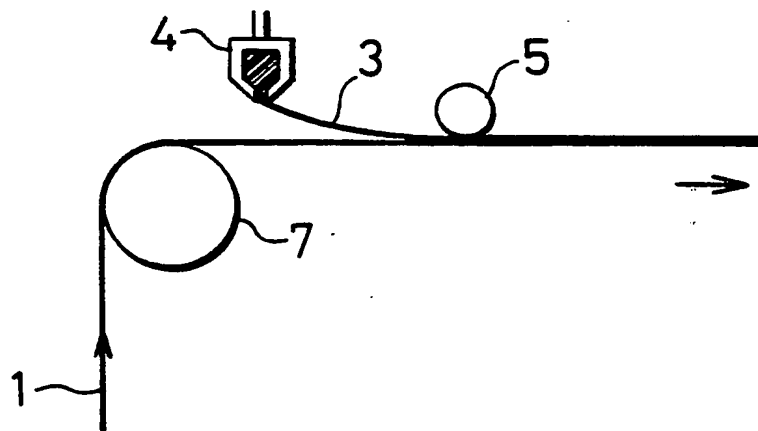
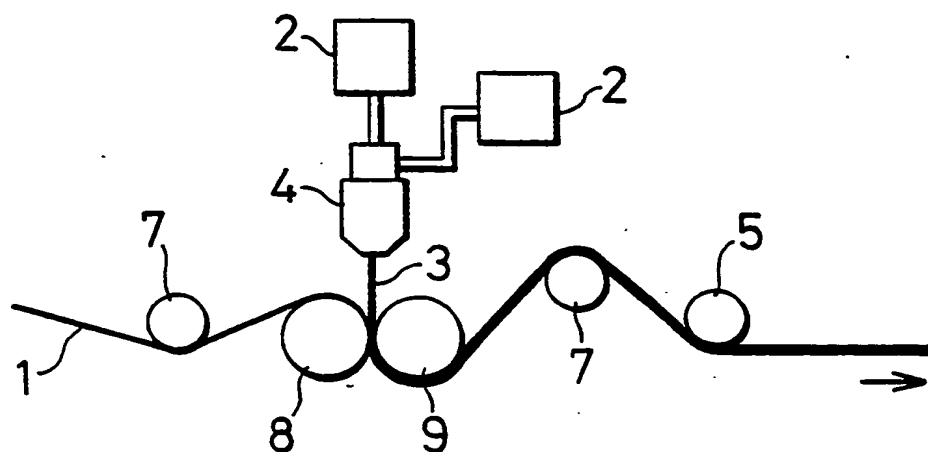


FIG. 3





European Patent
Office

EUROPEAN SEARCH REPORT

0067060

Application number

EP 82 30 2919

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	DE-A-1 504 109 (CONTINENTAL CAN COMP.) * Page 10, lines 13-23; page 11; page 12, lines 1-15; page 17, lines 1-5, 11; figure *	1,8-10	B 05 D 1/26 B 05 D 7/14 B 32 B 15/08 B 32 B 31/30
A	--- JAPANESE PATENTS REPORT, vol. 74, no. 34, Derwent Publications Ltd., London, G.B. & JP - A - 74 030 697 (YAMAYO KOKUTEIKI K.K.) 15-08-1974	1,2,10	
A	--- GB-A-1 566 422 (TORAY INDUSTRIES INC.) * Page 6, lines 10-32; page 12, example 3 *		
A	--- US-A-3 547 682 (L.F.E. NIXON) * Column 2, lines 7-60; column 4, claim 6; figure *		
	-----		TECHNICAL FIELDS SEARCHED (Int. Cl. 3) B 05 D B 32 B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21-09-1982	Examiner VAN THIELEN J.B.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			

THIS PAGE BLANK (USPTO)